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THIOSILANE SYNTHETIC LUBRICANTS

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This invention relates, broadly, to synthetic lubricants having a desirable combination of properties, namely, viscosities within the lubricating oil range, low pour points, high viscosity indices, and good stability. It is more particularly concerned with mixed orthothiosilicate esters having the aforementioned desirable combination of properties.

Mixed orthothiosilicate esters are the reaction products obtained from the reaction involving a total of four moles of at least two different thiols and about one mole of silicon tetrachloride. For example, the reaction might involve about one mole of octanethiol and about three moles of dodecanethiol and one mole of silicon tetrachloride; or, about one mole of thiophenol and about three moles of octanethiol and one mole of silicon tetrachloride.

The range of variation of viscosities of lubricating oils is well known to those skilled in the art. Ordinarily, the viscosity of lubricating oils varies between about 18 centistokes and about 500 centistokes, in terms of kinematic viscosity at 100° F.

The preparation of tetraalkylorthothiosilicates in general, has been described by Backer and Stienstra [Rec. Trav. Chim., 51, 1197 (1932); *ibid.*, 52, 912 (1933); *ibid.*, 54, 38 (1935)] and by Klasens and Backer [Rec. Trav. Chim., 58, 941 (1939)]. The tetraalkylorthothiosilicates, however, are wanting in one or more of the aforementioned desirable characteristics. Viscosity indices and stability are usually good, but the viscosities are low and the pour points, generally, are high. The tetraalkylorthothiosilicates having at least two different alkyl groups present in the molecule still show no improvement with respect to the aforementioned desirable characteristics. In fact, the viscosities decrease and the pour points are higher, as will be illustrated hereinafter.

In accordance with the present invention, it has now been discovered that it is possible to prepare mixed orthothiosilicate esters possessing a combination of all of the desirable properties mentioned hereinbefore. It has now been found that the reaction products obtained from the reaction involving about three moles of an alkanethiol reactant, about one mole of a cyclic thiol, and about one mole of a silicon tetrahalide, constitute excellent synthetic lubricants having viscosities falling within the viscosity range of lubricating oils, low pour points, high viscosity indices, and good stability.

Accordingly, it is an object of the present in-

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vention to provide synthetic lubricants which are relatively inexpensive. Another object is to provide new orthothiosilicate ester types of synthetic lubricants. A more specific object is to provide orthothiosilicate ester types of synthetic lubricants having viscosities falling within the viscosity range of lubricating oils, low pour points, high viscosity indices, and good stability. Other objects and advantages of the present invention will become obvious to those skilled in the art from the following detailed description.

Broadly stated, the present invention provides new synthetic lubricants having viscosities falling within the viscosity range of lubricating oils, low pour points, high viscosity indices, and good stability, which comprise the reaction products obtained from the reaction involving about three moles of an alkanethiol reactant, about one mole of a cyclic thiol, and about one mole of a silicon tetrahalide, the total number of carbon atoms and heterocyclic atoms present in three moles of the alkanethiol reactant and one mole of the cyclic thiol reactant varying between about 20 and about 40 and, preferably, between about 24 and about 34.

The thiol reactants utilizable for preparing the synthetic lubricants of the present invention include the alkanethiols and the cyclic thiols, i. e., cycloalkanethiols, arylthiols, and heterocyclic thiols. As stated hereinbefore, three moles of the thiol reactants involved in the reaction must be alkanethiols. Non-limiting examples of the alkanethiol reactants suitable for the purposes of the present invention are propanethiol-1, propanethiol-2, butanethiol-1, 2-methylpropanethiol-1, pentanethiol-1, 2-methylbutanethiol-4, hexanethiol-1, octanethiol-1, 2-ethylhexanethiol-1, decanethiol-1, and dodecanethiol-1. The three moles of the alkanethiol reactant may be furnished by a single alkanethiol, by two different alkanethiols, or three different alkanethiols. The fourth mole of the four moles of thiol reactants involved in the reaction may be a cycloalkanethiol, an arylthiol, or a heterocyclic thiol. Non-limiting examples of the cycloalkanethiol reactant are cyclohexanethiol, cyclopentanethiol, and methylcyclohexanethiol. The arylthiol reactants utilizable herein are, for example, thiophenol, o-tolylthiol, m-tolylthiol, p-tolylthiol, benzylthiol, α -naphthylthiol, and β -naphthylthiol. Thienylthiol-2, thienylthiol-3, 2-ethylthienylthiol-3, and pyridylthiol-2 may be mentioned by way of non-limiting examples of the heterocyclic thiol reactant. The thiols may be prepared in many different ways, as is well known

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to those skilled in the art, and many are available in commercial quantities.

The number of carbon atoms and heterocyclic atoms present in the thiol reactants is limited solely by the requirement, mentioned hereinbefore, that the sum of the number of carbon atoms and heterocyclic atoms in three moles of the alkanethiol reactant and one mole of the cyclic thiol reactant must be between about 20 and about 40, and, preferably, between about 24 and about 34. For example, if the alkanethiol reactant employed is octanethiol-1, there will be a total of 24 carbon atoms in three moles of the reactant. Then, in order to fall within the aforementioned number of carbon atom and heterocyclic atom limits, the fourth mole of cyclic thiol reactant must contain no more than 16 carbon atoms and heterocyclic atoms and, preferably, no more than 10 carbon atoms and heterocyclic atoms.

The silicon tetrahalide reactants utilizable herein are silicon tetrachloride, silicon tetrabromide, silicon tetraiodide, and silicon tetrafluoride. Of these, silicon tetrachloride and silicon tetrabromide are especially preferred.

The thiol reactants are reacted with the silicon tetrahalide reactant in a proportion of about three moles of alkanethiol and about one mole of a cyclic thiol for each mole of silicon tetrahalide reactant. For practical reasons, it is preferable to carry out the reaction in a non-polar hydrocarbon solvent. Especially preferred for this purpose are the aromatic hydrocarbon solvents, such as, for example, benzene, toluene, and xylene. The amount of solvent to be used will vary between about 5 per cent and about 50 per cent, based on the total weight of the reactants.

The temperature of the reaction is not too critical a factor. In general, the temperature will be the reflux temperature of the solvent used, and preferably, it varies between about 80° C. and about 140° C. The time of the reaction will depend upon the temperature employed. In practice, the reaction is complete after heating the reaction mixture, at the preferred temperatures, for a period of time varying between about two hours and about six hours, after all reactants have been added.

The reaction between the thiol reactants and the silicon tetrahalide reactant may be carried out by either of two methods, with equal effectiveness.

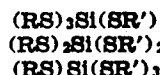
In the first method, the thiol reactants, in solution in a non-polar hydrocarbon solvent, are reacted with metallic sodium to form a suspension of the sodium salts of the thiol reactants. These sodium salts are then reacted with the silicon tetrahalide reactant to form the corresponding sodium halide which is filtered off. In the second method, the thiol reactants are reacted with the silicon tetrahalide reactant in the presence of an amine or a basic nitrogen compound. The amine combines with the hydrogen halide evolved during the reaction to form an insoluble amine hydrohalide. This is subsequently removed by conventional methods of separation, such as filtration and decantation. Amines and basic nitrogen compounds utilizable for this purpose are the trialkylamines having between one and five carbon atoms per alkyl radical. Non-limiting examples are triethylamine, trimethylamine and N-methylpiperidine. At least four moles of amine should be employed for each mole of silicon tetrahalide used in the reaction.

Regardless of the method used, the desired re-

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action product is isolated by distilling off, under reduced pressure, excess thiol reactants, any unreacted silicon tetrahalide, and the nonpolar hydrocarbon solvent. The desired synthetic lubricant product is recovered as the residue from the distillation operation.

The synthetic lubricant products contemplated herein are not individual compounds, but rather, mixtures of compounds. Thus, if the alkanethiol reactant is represented by the formula (RS)H, wherein R is an alkyl radical, and the cyclic thiol reactant is represented by the formula (R'S)H, wherein R' is a cyclic radical, the products obtained will comprise mixtures of the following three compounds:



The following specific examples are for the purpose of illustrating modes of preparing the orthothiosilicate esters contemplated in the present invention, and for the purpose of demonstrating the advantages thereof as synthetic lubricants. It is to be clearly understood that the invention is not to be limited to the specific thiol reactants and silicon tetrahalide reactant, or to the operations and manipulations described in the examples. As will be apparent to those skilled in the art, other reactants, as set forth hereinbefore, may be used to prepare a wide variety of products in accordance with this invention.

EXAMPLE I

A mixture consisting of 80.3 grams of octanethiol-1, 12.6 grams of metallic sodium, and 300 cubic centimeters of benzene was heated to and kept at reflux temperature (about 80° C.) until all of the sodium had reacted. A solution of 22 grams of silicon tetrachloride in 22 cubic centimeters of benzene was slowly added to the resultant slurry of sodium mercaptide while stirring. After addition was complete, the reaction mixture was refluxed (80° C.) for three hours, cooled to room temperature (25° C.), and filtered to remove sodium chloride and solid impurities. The filtrate was subjected to distillation at a temperature of 250° C. under a pressure of one millimeter, to remove benzene and unreacted materials. The residue was filtered through filtering clay, and a filtrate weighing 52 grams was obtained. The product contained 20.6 per cent sulfur (calculated for $\text{C}_{31}\text{H}_{66}\text{S}_4\text{Si}$; S=21.1 per cent). The pertinent properties of this product are set forth in Table I.

EXAMPLE II

A mixture of two moles of sodium-n-octyl mercaptide and two moles of sodium-n-dodecyl mercaptide was reacted with one mole of silicon tetrachloride. The reaction was completed and the product was isolated in the same manner as set forth in Example I. The product contained 18.5 per cent sulfur (calculated for $\text{C}_{46}\text{H}_{98}\text{S}_4\text{Si}$; S=17.8 per cent). Pertinent properties of this product are tabulated in Table I.

EXAMPLE III

To a solution of 11.8 grams of thienylthiol-3 and 17.0 grams of silicon tetrachloride in 200 cubic centimeters of benzene, 20 grams of triethylamine were introduced dropwise. After one hour, 61 grams of decanethiol-1 were added, and then 61 grams of triethylamine were added drop-

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wise. After addition was complete, the reaction mixture was held at reflux temperature (about 80° C.) for about two hours. The solution was filtered and the product was isolated in the manner described in Example I. Physical data of the product are set forth in Table I.

EXAMPLE IV

A mixture of 33 grams of thiophenol, 85 grams of silicon tetrachloride, and 250 cubic centimeters of xylene was reacted in the presence of 36 grams of triethylamine. After the vigorous reaction had subsided, the excess silicon tetrachloride was distilled off. The solution was filtered and the filtrate was returned to the reaction vessel. Then, 116 grams of octanethiol-1 were added, and 120 grams of triethylamine were added dropwise. The reaction mixture was heated at reflux temperature (about 135° C.) for about two hours, and filtered. 35 grams of octanethiol-1 and 35 grams of triethylamine were then added to the filtrate. The latter was then heated to and held at the reflux temperature of the reaction mixture (135° C.) for about two hours. The synthetic lubricant product was isolated in the manner set forth in Example I. The pertinent physical data of the product are set forth in Table I.

EXAMPLE V

A solution of 11.6 grams of cyclohexanethiol and 17.0 grams of silicon tetrachloride in 300 cubic centimeters of xylene was reacted by adding slowly 20 grams of triethylamine. There was an immediate precipitation and an evolution of heat. The reaction mixture was stirred and heated at reflux temperature (about 135° C.) for about one hour. Then, 48 grams of octanethiol-1 were added, followed by the addition, dropwise, of 50 grams of triethylamine. The reaction mixture was heated to and held at reflux temperature (135° C.) for an additional four hours. The synthetic lubricant product was obtained in the manner described in Example I. Physical data of this product are set forth in Table I.

Table I

Example	Viscosity (cs.)		Viscosity Index	Pour Point, ° F.
	@ 100° F.	@ 210° F.		
I.....	16.40	3.97	163	-15
II.....	12.08	3.30	164	+50
III.....	30.57	6.39	156	-15
IV.....	18.91	4.39	164	-20
V.....	25.91	5.26	156	<-65

From the data set forth in Table I, it will be apparent that the reaction product obtained by reacting four moles of an alkanethiol, octanethiol-1, with one mole of silicon tetrachloride (Example I) provides a synthetic lubricant which lacks one of the necessary characteristics, namely, a viscosity falling within the viscosity range of lubricating oils. When two different alkanethiols are used (Example II), no improvement is obtained. In fact, the viscosity decreases and the pour point increases tremendously. On the other hand, reaction products prepared by the reaction involving three moles of an alkanethiol reactant, one mole of a cyclic thiol, and one mole of silicon tetrachloride, in accordance with the present invention, provide synthetic lubricants having viscosities falling within the viscosity range of lubricating oils, high viscosity indices, and low pour points.

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The stability of the synthetic lubricants prepared in accordance with the present invention is illustrated by the data set forth in Table II. These data were obtained by comparing the product of Example III with an SAE 10 motor oil in a laboratory bench-scale oxidation test.

Table II

Sample	N. N. ¹	Viscosity Increase, Per Cent	Oil Loss, Per Cent	Sludge
Example III.....	2.8	33.7	4	Slight.
SAE 10 Oil.....	15.0	95.0	5	Do.

¹ Neutralization number=mg. KOH required to neutralize 1 gram of oil sample.

In this test, a 50-milliliter sample of test oil is placed in a test tube containing an oxidation catalyst comprising one square inch of iron and three square inches of copper. The tube is placed in a constant-temperature bath kept at a temperature of about 300° F. A gas-delivery tube is inserted into the oil and dry air is passed through the oil at a rate of five liters per hour. After 48 hours, the tube is removed and examined for sludge. The sludging of the oil is a criterion of the tendency of the lubricant to form insoluble substances, organic and inorganic. The viscosity increase reveals the tendency of the lubricant toward polymerization. The neutralization number is a measure of the susceptibility of the lubricant to oxidize to acidic substances. The formation of volatile oxidation products is indicated by the percentage oil loss.

From the data set forth in Table II, it will be apparent that the synthetic lubricants of the present invention are superior to mineral lubricating oils. They are not susceptible to oxidation, there is little tendency toward polymerization and, finally, there is very little formation of acidic bodies.

In addition to their utility as synthetic lubricants, per se, the products of the present invention are, as a class, completely miscible in mineral lubricating oils. Accordingly, they can be used as extenders for lubricants, or as additives to lubricating oils for the purpose of imparting desirable properties thereto. In view of their stability, the products contemplated herein are also useful as heat transfer agents.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

We claim:

1. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, consisting essentially of the reaction product obtained by reacting a cyclic thiol selected from the group consisting of cycloalkane-thiols, arylthiols, thienylthiol-2, thienylthiol-3, 2-ethylthienylthiol-3, and pyridylthiol-2, at least one alkanethiol, and a silicon tetrahalide, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms and heterocyclic atoms present in said cyclic thiol and said alkanethiol varying between 20 atoms and 40 atoms.

2. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting a cycloalkanethiol, at least one alkanethiol, and a silicon tetrahalide, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms present in said cycloalkanethiol and said alkanethiol varying between 24 carbon atoms and 34 carbon atoms.

3. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting an arylthiol, at least one alkanethiol, and a silicon tetrahalide, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and 140° C.; the total number of carbon atoms present in said arylthiol and said alkanethiol varying between 24 carbon atoms and 34 carbon atoms.

4. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting a heterocyclic thiol selected from the group consisting of thienylthiol-2, thienylthiol-3, 2-ethylthienylthiol-3, and pyridylthiol-2, at least one alkanethiol, and a silicon tetrahalide, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms and heterocyclic atoms present in said heterocyclic thiol and said alkanethiol varying between 24 atoms and 34 atoms.

5. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, consisting essentially of the reaction product obtained by reacting a cyclic thiol selected from the group consisting of cycloalkanethiols, arylthiols, thienylthiol-2, thienylthiol-3, 2-ethylthienylthiol-3, and pyridylthiol-2, at least one alkanethiol, and silicon tetrachloride in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms and heterocyclic atoms present in said cyclic thiol and said alkanethiol varying between 20 atoms and 40 atoms.

6. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting a cycloalkanethiol, at least one alkanethiol, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms present in said cycloalkanethiol and said alkanethiol varying between 24 carbon atoms and 34 carbon atoms.

7. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting an arylthiol, at least one alkanethiol, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and 140° C.; the total number of carbon atoms present in said arylthiol and said alkanethiol varying between 24 carbon atoms and 34 carbon atoms.

8. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting a heterocyclic thiol selected from the group consisting of thienylthiol-2, thienylthiol-3, 2-ethylthienylthiol-3, and pyridylthiol-2, at least one alkanethiol, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.; the total number of carbon atoms and heterocyclic atoms present in said heterocyclic thiol and said alkanethiol varying between 24 atoms and 33 atoms.

9. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting cyclohexanethiol, octanethiol-1, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.

10. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting thiophenol, octanethiol-1, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.

11. A synthetic lubricant having a viscosity falling within the viscosity range of lubricating oils, a low pour point, a high viscosity index, and good stability, which consists essentially of the reaction product obtained by reacting thienylthiol-2, decanethiol-1, and silicon tetrachloride, in a proportion of about one mole, about three moles, and about one mole, respectively, and at a temperature varying between about 80° C. and about 140° C.

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REFERENCES CITED

The following references are of record in the file of this patent:

Klasen et al.: "Recueil de Trav. Chimique," vol. 61 (1942), pp. 513-522.

Certificate of Correction

Patent No. 2,562,474

July 31, 1951

BERNARD A. ORKIN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 23, and column 8, line 10, before "140° C." insert *about*;
column 8, line 28, for "33 atoms" read $3\frac{1}{2}$ atoms;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of January, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.